AFOSR-TR. 89-0100

FRACTURE AND HARDNESS CHARACTERISTICS OF SEMICONDUCTOR ALLOYS

Final Report

November 1988

By: M.A. Berding, Research Physicist
A. Sher, Associate Director
M. van Schilfgaarde, Research Physicist
Physical Electronics Laboratory

An-Ban Chen
Auburn University

DTIC
ELECTE
FEB 2 1 1989
H

89 2 16 086

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	None

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
	AFOSR-TR- 89-0100

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
SRI International		AFOSR/NE

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
333 Ravenswood Avenue Menlo Park, California 94025	Building 410 Bolling Air Force Base Washington, D.C. 20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Air Force Office of Scientific Research	8b. OFFICE SYMBOL (If applicable) AFOSR/NE	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
		F49620-85-0023

8c. ADDRESS (City, State, and ZIP Code) Attn: Dr. Cole Litton	10. SOURCE OF FUNDING NUMBERS			
Building 410 Bolling Air Force Base Washington, D.C. 20332-6448	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
	61102F	2306	61	

11. TITLE (Include Security Classification)

Fracture and Hardness Characteristics of Semiconductor Alloys

12. PERSONAL AUTHOR(S)

M.A. Berding, A. Sher, M. van Schilfgaarde, An-Ban Chen

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 01 Sep 85 TO 31 Aug 88		

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Hardness, Coulomb energies, semiconductor alloys.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

We have studied the properties of semiconductor compounds and alloys as they relate to the mechanical and structural behavior of the materials. We have calculated the deviations from randomness including contributions from strain, chemical and Coulomb energies. Surfaces have been examined and substantial surface segregation is found to occur in several alloy systems. Extraction energies in the alloys are found to be very sensitive to the alloy environment and may have important consequences on diffusion. An effective medium theory of the bulk modulus has been developed and show that the bulk modulus varies nearly linearly with alloy composition. Finally the Sher model of hardness has been improved by the inclusion of the dissipative term arising from the Peierls stress in the lattice.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Litton		NE

DD Form 1473, JUN 86 — *Previous editions are obsolete.* —

CONTENTS

ILLUSTRATIONS

TABLES

I INTRODUCTION

The mechanical properties of metals have long been of interest because of their use as structural materials. Even so, much of the understanding of the mechanical properties of metals is from empirical data and macroscopic models. In semiconductors, structural properties are also of interest because of their relationship to the material's manufacturability, as well as the impact that structural defects, such as dislocations and vacancies, may have on electronic properties. Thus, we strive for a microscopic understanding of the mechanical/structural properties of the semiconductors, by relating the observed macroscopic structural properties to microscopic quantities such as bond lengths and energies, elastic constants, and so on. It is only through a microscopic understanding of the mechanical behavior of semiconductors that we can fully understand the driving mechanisms of structurally inferior materials and devise new ways to improve their characteristics—for example, by alloying, varying the growth techniques, and so on. Additionally, new nonequilibrium growth techniques of semiconductor alloys may result in material possessing long- or short-range ordering, which in turn will influence the mechanical properties of these alloys. Only from a microscopic theory of the mechanical properties of the materials can the mechanical properties of these novel new materials be understood.

The remainder of this report is organized as follows: In Section II, our work relating to correlations and ordering in semiconductor alloys is summarized. In Section III, results of the calculations of vacancy formation energies and surface segregation in zinc-blende semiconductor compounds and alloys are summarized. Our work on the elastic constants, hardness, and cleavage is summarized in Section IV. Note that only a brief summary of the accomplished work is presented in cases where details can be found in our published materials, which are listed as references following the conclusion of the text. A bibliography of publications supported in whole or in part by this contract follows the references.

II CORRELATIONS AND ORDERING IN SEMICONDUCTOR ALLOYS

The state of order or disorder in semiconductor alloys and its dependence on growth method and growth and processing parameters is important in understanding the structural properties of these materials. The first step towards such an understanding is therefore a knowledge of the driving forces for order and disorder. We have developed a quasichemical approximation to study effects that drive short-range order in the pseudobinary alloys. The complementary situation of alloys with long-range order has also been calculated. The calculations for the short- and long-range ordered alloys include contributions to the total energy from chemical and strain terms. One further contribution to the total energy comes from Coulomb energies in the alloys, which may differ substantially in the ordered structures and the random alloys. Our calculations show that the Coulomb energy contribution to the mixing energies is, in general, small, although in some lattice matched systems where the usual dominant strain energy is small, Coulomb energies may dominate. What follows is a brief summary of our work in the area. General conclusions are included in Section V.

A. Quasichemical Approximation in Pseudobinary Alloys

The quasichemical approximation for an $A_{1-x}B_x$ alloy has been formulated for an arbitrary lattice and choice of cluster.[1] The statistical problem of the average number of each class of clusters is collapsed into a polynomial equation. An n-atom cluster of type j is characterized by an excess energy ε_j, the number of B atoms $n_j(B)$, and the degeneracy g_j. If ε_j is a linear function of $n_j(B)$, and g_j is a binomial coefficient of n and $n_j(B)$, then the cluster populations will be random. Strains due to lattice-size mismatches, chemical (electron-ion interaction) differences, and differences between the electron-electron Coulomb interactions of the alloy constituents will drive nonlinear variations of ε_j on $n_j(B)$. The g_j is modified by coherent, eternally applied stresses and temperature gradients present during crystal growth. The conditions under which compounds are formed or spinodal decomposition occurs have been derived. The possibility of materials consisting of arrays of two kinds of domains, one a random alloy and the other an ordered compound have been considered. The theory has been specialized to pseudobinary semiconductor alloys $A_{1-x}B_xC$ in a distorted zinc-blende structure. Results for many systems have been published.[1-6]

2

The generalized quasichemical approximation we have developed has been used to study the phase diagram of several pseudobinary alloys.[5,7] The solid mixing free energies were calculated from the generalized quasichemical approximation,[1] while the liquid mixing free-energies were constructed using the quasichemical approximation method of Stringfellow and Greene.[8] Knowing the free-energies, the liquidus and solidus concentrations for a given temperature were calculated by the common tangent method equivalent to matching the chemical potential for the liquid and solid phases. The calculated liquidus and solidus curves for the alloys considered, GaInP, GaInAs, InSbAs, HgCdTe, HgZnTe, and CdZnTe are in good agreement with experiment.

B. Binding Energies and Bond Lengths in Ordered Structures

At least four pseudobinary alloys, AlGaAs, GaInAs, GaInP, and GaAsSb grown from MBE and MOCVD have been found to have the long-range ordering (LRO). From a technology point of view, the LRO has not produced unusually electrical or mechanical properties that deserve special attention, mainly because the degree of LRO is rather weak and the ordering only occurs under very special growth conditions. However, the LRO may provide some clue for a better understanding of growth processes and the structural properties of these epitaxially grown systems as compared to the bulk alloys.

Whether or not the alloys with LRO are in thermal equilibrium states may be difficult to test. One possible test is a simple annealing experiment. If the LRO is restored after heating to temperatures above the transition temperature and then cooled down slowly, the alloy will be in an equilibrium state. If not, the LRO may be metastable. The difficulty in this experiment is the rates of diffusion at the temperature near the order-disorder transition. If diffusion rates are slow here, the time necessary to restore the LRO may be extremely long (effectively infinite). An accurate calculation of the total energies can give an insight into this problem. Below, we describe our unpublished results to date for such a calculation.

Our calculation is based on the first-neighbor tight-binding model. The total energy is the sum of the electron energies in the valence bands, E_{el}, and the nearest-neighbor repulsive pair energies, V_0. There are two major differences between our calculation and Harrison's bond-orbital model. First, we have to calculate the band structures for the appropriate structures, i.e., zinc blende (zb), copper-gold I (CuAu I), and the chacopyrite (cp) structures, and then perform the Brillouin-zone summation (BZ) to obtain E_{el}. The second difference is that we have

3

adjusted the values and the scaling rules for the interaction parameters and V_o to improve the agreement between the calculated quantities and the experimental values for the constituent compounds as listed in Table 1.

With four s and p orbitals per atom, the sizes of the Hamiltonian matrix for a given k in the BZ are, 16 × 16, and 32 × 32 respectively for the CuAu I and cp structures. A uniform grid of 125 K points inside the BZ are used to obtain E_{el}. The total energy for a given system is calculated at four guessed lattice parameters α, or a given α at four internal distortion parameters; these results are used to locate the equilibrium bond lengths, d_1 and d_2, and the minimum energy. As an example, Figure 1 shows the energy per bond, E_b, as a function of the average bond length, d, for GaAs, InAs, and InGaAs calculated in the CuAu I structure. Table 2 lists the equilibrium values of d, d_1, d_2, E_b, two kinds of excess energies, ΔE and $\Delta E'$, to be discussed below, and the bulk moduli B for three ordered ternary alloys in the CuAu I and cp structures. Some key results are summarized as follows:

(1) The average $d = (d_1 + d_2)/2$ obeys Vegard's law very well.

(2) The calculated d_1 and d_2 fall in the range of experimental bimodal distributions found for the bulk pseudobinary alloys.

(3) The alloy bulk moduli are a few percent smaller than the average values of the constituent compounds.

(4) All the ternary alloys have positive excess energies, defined as $\Delta E = 4E_b$ (ABC) $- 2E_b$ (BC), where E_b (AC) and E_b (BC) are the bond energies of the constituent compounds. The ΔE values are larger in the CuAu I than in the cp structures for the cation-substituted alloys such as InGaAs, the opposite is found for GaAsSb.

(5) All ordered alloys have very substantial negative excess energies, $\Delta E'$, which is defined similarly to the ΔE except that energies of the two constituent compounds are evaluated at a lattice constant constrained to be that of the substrates.

Table 1

CALCULATED AND EXPERIMENTAL* VALUES
FOR SIX REPRESENTATIVE COMPOUNDS

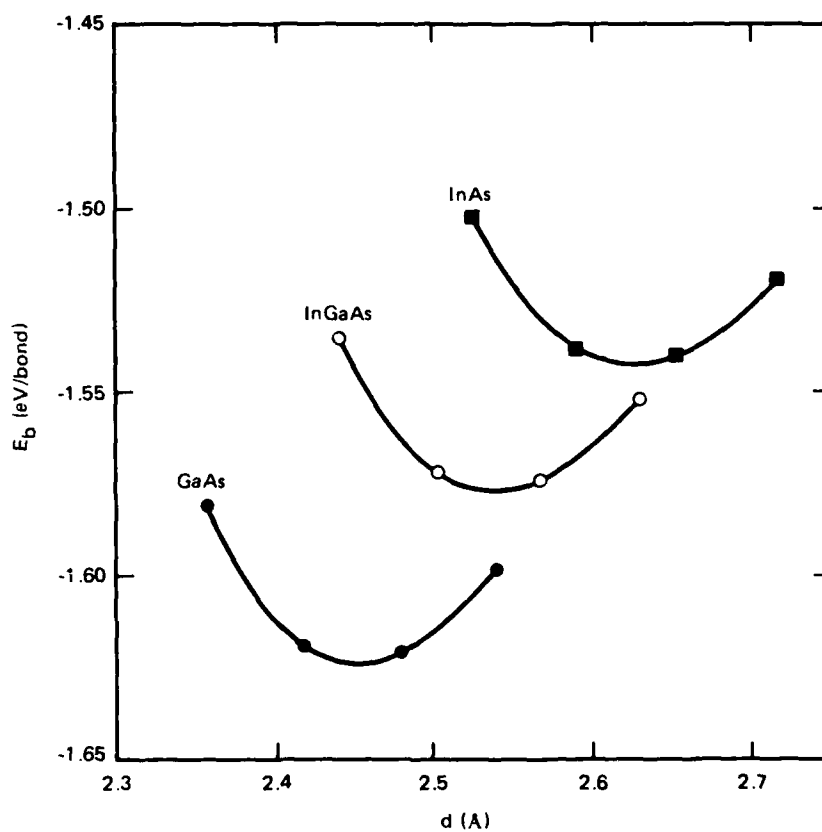|	AlAs	GaP	GaAs	GaSb	InP	InAs
d (Å)	2.453	2.360	2.450	2.642	2.541	2.625
E_b (eV)	-1.8840 (-1.89)	-1.7722 (-1.78)	-1.6239 (-1.63)	-1.4764 (-1.48)	-1.7406 (-1.74)	-1.5421 (-1.55)
B (10^{11} dynes/cm^2)	7.860 (7.73)	8.836 (8.87)	7.555 (7.48)	5.919 (5.63)	7.466 (7.25)	5.823 (5.80)

*Experimental values are shown in parenthesis.

4

FIGURE 1   BOND LENGTH DEPENDENCE OF BOND ENERGY
IN GaAs, InAs, AND $In_{0.5}Ga_{0.5}As$ WITH THE CuAu I
STRUCTURE

The last two results are the most relevant to the order-disorder transitions. For a bulk alloy, the ΔE is a measure of the mixing enthalpy, and the disordered alloy will be immiscible below the critical temperature, $T_c = \Delta E/k$. Our results are in agreement with what we found in our detailed studies of the statistics and phase-diagrams of the bulk alloys. However, for an epitaxially grown alloy on a lattice matched substrate (e.g., GaInAs and GaAsSb grown on InP, and GaInP grown on GaAs), the energies $\Delta E'$ are the appropriate excess energies. Since $\Delta E'$ are all negative, (see Table 2) these alloys will be in the ordered states at a temperature below the order-disorder transition temperature, given roughly by $T_0 = |\Delta E'|/2k$. The temperatures T_0 associated with the tabulated $\Delta E'$ are very close to the range of the substrate temperatures at which the LRO were found to exist in these alloys. This may be a mechanism for the LRO in these alloys. However, this mechanism is not the only driving force for the LRO. For the GaAlAs system, the calculated excess energy is essentially zero, because GaAs and AlAs are almost lattice matched. Likewise, we are also puzzled by the difficulty in the growth

5

Table 2

CALCULATED VALUES FOR THREE ORDERED TERNARY ALLOYS

	InGaAs		InGaP		GaSbAs	
	CuAu I	cp	CuAu I	cp	CuAu I	cp
d (Å)	2.537	2.536	2.454	2.452	2.550	2.552
d_1 (Å)	2.602	2.609	2.523	2.530	2.627	2.616
d_2 (Å)	2.476	2.467	2.389	2.380	2.447	2.492
E_b (eV)	-1.5762	-1.5775	-1.7431	-1.7456	-1.5451	-1.5412
ΔE (meV)	27	22	33	23	19	35
$\Delta E'$ (meV)	-92	-87	-106	-96	-130	-120
B (10^{11}dynes/cm^2)	6.567	6.599	7.992	8.028	6.195	6.111

of HgCdTe and the experimental findings regarding the large clustering effects despite all the mechanisms that we know of that give a very small mixing enthalpy and indicate that HgCdTe should behave like a random alloy.

C. Coulomb Energies

A scheme has been developed to calculate the configuration dependence of the Coulomb electron-electron interactions in tetrahedrally coordinated pseudobinary alloys of the form $A_{0.5}B_{0.5}C$.[9,10] Coulomb energies have been calculated for three configurations: a random alloy configuration, an ordered sublattice in the Cu-Au structure, and a spinodally decomposed configuration. The Coulomb energies, driven by a bond polarity mismatch, must be considered as a contribution to the mixing enthalpy in semiconductor alloys in addition to the strain (driven by bond length mismatch) and chemical terms usually considered. The results of the calculations show that the ordered structures have a lower Coulomb energy than the random alloys. This is because, in the absence of long-range order, the random alloy does not benefit from a Madelung enhancement of the electrostatic energy gained from a coherent sum of alternating charges. The Coulomb energy terms are most important in the mixing enthalpy for lattice matched systems (e.g., AlGaAs, where experimental evidence of ordering has been observed).[11] Note that a factor of two errors was made in van Schilfgaarde's papers[9,10] and these published mixing energies are a factor of two too large.

6

III VACANCIES AND SURFACE SEGREGATION IN SEMICONDUCTORS

A. Vacancy Formation Energies

Vacancies can affect the structural properties of semiconductors in several ways. First, the presence of vacancies during high-temperature bulk growth may form vacancy clusters and precipitate into dislocation loops. Second, the presence of vacancies is important in both self- and impurity-diffusion processes, and in some systems are, therefore, related to the efficiency of annealing and doping. Finally, dislocation motion may be sensitive to the presence of vacancies, via climbing processes, whereby vacancies are absorbed or emitted and through an electrical interaction between dislocations and vacancies, as in the case of charged vacancies. Our work relating to the calculation of the total energies of vacancy formation in the zinc-blende compound and alloy semiconductors is summarized below; general conclusions are included in Section V.

Vacancy formation energies in the semiconductor compounds have been calculated using a tight-binding cluster model.[12-14] Corrections from lattice bond length relaxation and charge redistributions about the vacancy site have been included. Two final states for the removed atom have been considered corresponding to a free atom state in vacuum and to the removed atom at a triply bonding site on a (111) surface, and a doubly bonding site on a (100) surface. Cluster convergence has been examined by comparing to Green's function calculation that treats interaction to infinite range. The cluster method is advocated over Green's-function method, because it allows a detailed description of the vacancy formation energies in alloys.

Vacancy formation energies in pseudobinary semiconductor alloys of zinc-blende structure have been calculated using a modification of the cluster model developed for the compounds.[15] Twelve constituent atoms are considered (group III: Al, Ga, In; group V: P, As, Sb; group II: Zn, Cd, Hg; and group VI: S, Se, Te), and cation and anion extraction energies in all III-V and II-VI pseudobinary alloys formed from these constituents are calculated. The extraction energies are found to be sensitive to the class of cluster from which the atom is removed, with the removal of a cation being the most sensitive to the alloy environment in an anion substituted alloy, and likewise, the removal of an anion being the most sensitive to the alloy environment in a cation substituted alloy. In most random alloys, the extraction energies are

found to vary nonlinearly with alloy composition, and most often bow downwards, in some cases reaching a minimum at a finite alloy composition. Such nonlinearity in the extraction energies will be important (e.g., in the interpretation of diffusion and doping incorporation in some alloy systems). The present alloy results can be readily extended to vapor phase finals states, other than the free atom assumed for the extraction energies calculated here, by including the appropriate molecular phase energies and pressures. Moreover, the extraction energies can be directly related to the chemical potentials that drive interdiffusion between solids. This is especially important in understanding the stability of epitaxial layers on different substrates and of superlattices.

B. Surface Segregation

The driving forces for surface segregation in the alloys, whereby the surface may be rich in one of the constituent species, are related to the vacancy formation energies to the particular surface of interest. We have studied surface segregation in several systems, and a summary of this work is given below. The conclusions that we have drawn are discussed in Section V.

We have developed a theory of surface segregation for the pseudobinary semiconductor alloys.[16] Pseudobinary alloys of the form $A_{1-x}B_xC$ almost always have different surface concentrations from the bulk in order to maintain a constant chemical potential for each layer in the alloy. The enthalpy responsible for segregation is the difference in the energies for moving an A or B atom from the bulk alloy to the surface. There are two major contributions to this energy: (a) a bond-breaking mechanism, whereby the element with the lowest surface energy segregates to the top and (b) strain release, where the dilute element in the compound segregates to the surface to alleviate the strain energy due to mismatch of the AC and BC bond lengths. In our segregation model, the free energy of each layer is calculated in the regular and quasichemical approximations. By equating the chemical potentials of each successive layer to the bulk, the composition of each layer is obtained.

The degree of surface segregation for the alloys $Hg_{1-x}Cd_xTe$ (lattice matched) and $Hg_{1-x}Zn_xTe$ (lattice mismatched) have been calculated. Our results show that there is strong surface enrichment of Hg in $Hg_{1-x}Cd_xTe$, while there is less surface segregation of Hg in $Hg_{1-x}Zn_xTe$ at the low x values appropriate for infrared applications. Mercury segregation to the surface will lower the band-gap energy or may turn the surface into a semimetal, thereby affecting the passivation of the surface.

8

IV MECHANICAL PROPERTIES
OF SEMICONDUCTOR COMPOUNDS AND ALLOYS

A. Elastic Constants

It is customary to use a two-parameter force constant model such as the Keating model[17] in many calculations of the structure-related properties of the zinc-blende material; yet, three independent force constants are necessary to describe a general distortion for this crystal structure. We have developed an approximate, but *ab initio*, theory of the elastic constants in the tetrahedral semiconductors that provides a basis for the generation of empirical two-parameter force constant models[18,19] A relationship between the three independent force constants has been derived that is independent of the detailed form of the tight-binding matrix elements.

We have developed a theory for the internal strain energy and bulk modulus in semiconductor alloys.[20] The internal strain energy is shown to be governed by the square fluctuation of the bond lengths and an effective force constant that couples the atomic clusters to the environment. Analytical models show that the bulk moduli and bond lengths, as a function of concentration of these alloys, bow only slightly below the straight-line average. This work provides a basis of an effective-medium theory for calculating the input cluster energies in a statistical theory.

B. Hardness

Hardness has proven to be a useful probe of the mechanical properties of the brittle semiconductors. Here we will use the term hardness to refer specifically to Vickers' hardness, unless other wise noted. In the Vickers' hardness-measurement, a square pyramidal indenter is used and the hardness number is given by the applied load divided by the area of the indentation (i.e., units of pressure). Hardness has been found to be an intrinsic property of the material, because it is relatively independent of the applied load. One advantage of hardness measurements for semiconductors is that, unlike bending tests, only small samples are necessary for conventional Vickers' hardness-measurements, or for nanoindenter measurements, relatively thin epitaxial films can be probed. Additionally, unlike conventional tests used to

9

measure yield stress, hardness measurements can be made at room temperature, which is far below the usual plastic regime for most semiconductors. As such, the hardness measurement provides a convenient and usable probe.

The question remains, though, as to the interpretation of the hardness measurement in semiconductors; that is, just what property (or properties) of a semiconductor are we measuring when we measure hardness. In metals, an empirical relationship is found between the hardness, H, and yield stress, Y:

$$H = 3 Y \quad .$$

In metals, this relationship can be justified of the basis on continuum theory, as discussed in McClintock and Argon.[21] In semiconductors, such a simple relationship between H and Y is not necessarily appropriate for several reasons. During deformation in metals, many slip planes can be active because the Peierls barriers for dislocation motion in most directions are low. In contrast, because the bonds in semiconductors are strongly covalent, the Peierls barriers are high and dislocation in the (111) $\frac{1}{2}<\bar{1}10>$ slip system dominate.

To date, there is no complete quantitative theory of hardness in the semiconductors in which the temperature dependence, photoplastic effect, and the alloy hardening effect are included. Sher et al.,[22] proposed a model of hardness for the semiconductor compound that gives good quantitative agreement with experiment, but this model does not provide an explanation for several of the observed dependences of hardness. The Sher model of hardness in semiconductors differs from more conventional interpretations of hardness: In the Sher model, the hardness is dominated by dislocation-dislocation interactions, as opposed to dislocation activation and motion terms. We discuss our results of an improved quantitative model of hardness below.

1. Slip Systems

In the Sher hardness model, Vickers' hardness is found to be dominated by the interaction energy of an idealized array of dislocations that have been generated by the indenter. In their idealized array, no account was taken of the true slip systems active in the semiconductors. Experiments[23] have demonstrated that, in Vickers' hardness, slip occurs primarily on the {111} $\frac{1}{2} <\bar{1}10>$ glide set, where the three-fold symmetry of slip and rosette lines occur at the intersection of the {111} planes with the (111) surface.

10

For indentation on the (111) plane, dislocations can glide on the (111) plane parallel to the surface or on one of the three other {111} planes with a total of four active slip planes. Although the detailed analysis differs from that given previously,[22] the contribution to the hardness from the interaction energy is comparable to that previously calculated. This contribution to H is directly proportional to the shear coefficient.

2. Peierls Energy

The Peierls energy is difficult to calculate precisely because of dislocation charge effects and reconstruction at the dislocation core. In the context of the hardness measurement we wish calculate the Peierls energy to access the importance of this contribution to the Vickers' hardness number. Although it is generally agreed that dislocations in semiconductors move through the generation and propagation of double kinks, in the hardness measurement, the region about the indenter is grossly plastically deformed. Because the dislocation velocity is low at room temperature (see below), the large dislocation pile-up model proposed by Sher et al.,[22] may be appropriate. If the dislocation separation is small, dislocation motion through kink processes will be suppressed, and the dislocations will propagate as a complete unit.

To get from Configuration A to Configuration B in Figure 2, we must break a row of bonds. Since the long-range strain fields should be comparable in the two configurations as well as for intermediate configurations, the Peierls force can be calculated from local energy considerations only. The energy to break a bond at the dislocation core is approximately given by:

$$U_b = 2\sqrt{V_2^2 + V_3^2} + 2\varepsilon_{met} - V_0 + \frac{n}{4}\left[\varepsilon_h^a - \varepsilon_h^c\right]$$
(1)

where V_2 is the covalent energy, V_3 the ionic energy, ε_{met} the metallization energy, V_o the bond overlap energy, and ε_h^a and ε_h^c the hybrid energy for the anion and cation, respectively. The first two terms in Equation (1) account for the loss of the bonding energy of the two electrons in the breaking bond, the third term accounts for regaining the repulsive interaction energy of the bond, and the fourth term accounts for the energy gain to transfer electrons back from the cation to the anion. We note that the electron orbitals of the atoms at the dislocation

11

(a) CONFIGURATION A

(b) CONFIGURATION B
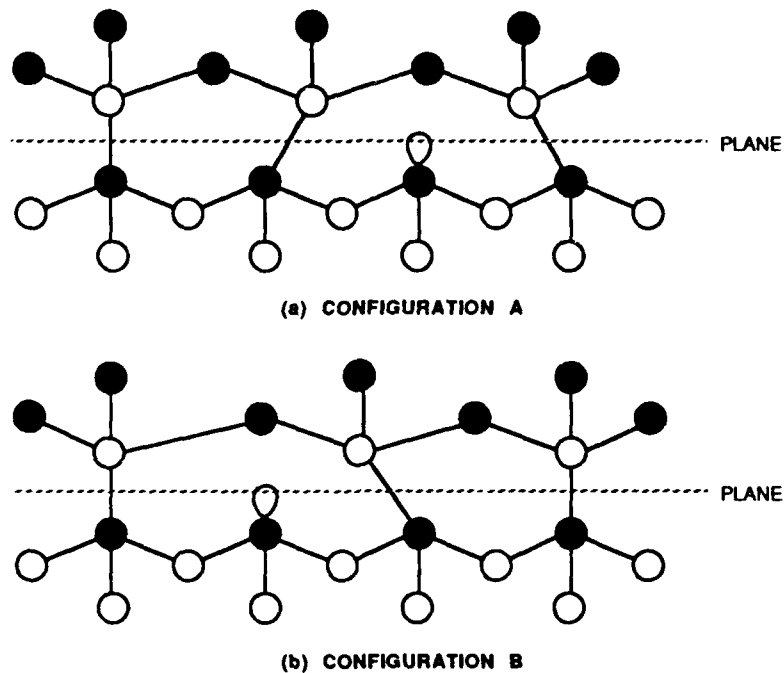
FIGURE 2   DISLOCATION MOTION ON THE SHUFFLE PLANE

core are left in the sp^3 hybrids after the bond breaking. The expression in Equation (1) represents a theoretical maximum of the Peierls energy, since no reconstruction at the core has been included.

To calculate the Peierls energy per unit length, we consider a primary dislocation in the $<\bar{1}10>$ direction in a zinc-blende compound. The number of bonds per unit length in $<\bar{1}10>$ is given by $1/b$ where b is Burger's vector. Thus, the Peierls energy per unit length is given by

$$E_P = \frac{U_b}{b} = \sqrt{\frac{3}{8}} \frac{U_b}{d} \quad , \tag{2}$$

where d is the bond length.

We can now calculate the Peierls force, or the force per unit length necessary to move a dislocation over the potential barrier, as illustrated in Figure 3. The Peierls energy is related to the Peierls force through
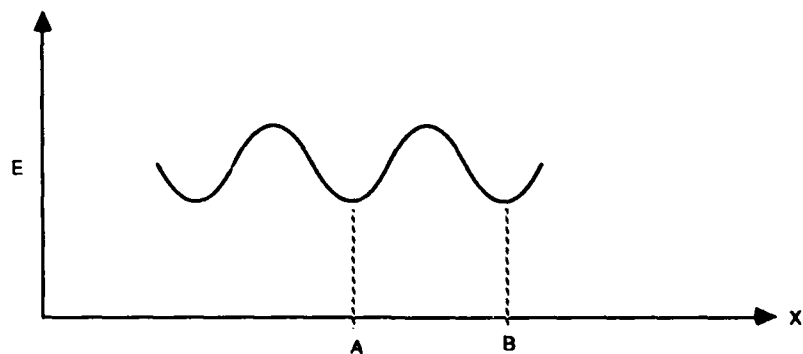
$$E_P = F_P L \qquad (3)$$

where

$$L = \frac{b}{2} \qquad (4)$$

is the distance between Configurations A and Configuration B. Solving for F_P in terms of U_b and d, we arrive at:

$$F_P = \frac{3}{4} \frac{U_b}{d^2} \quad , \qquad (5)$$

or

$$\tau_P = \sqrt{\frac{3}{2}} \frac{3}{8} \frac{U_b}{d^3} \quad . \qquad (6)$$

110388-0

FIGURE 3   POTENTIAL BARRIER FOR DISLOCATION MOTION

13

Values for U_b and τ_p are summarized in Table 3.

Table 3

CALCULATED PEIERLS STRESS AND HARDNESS
FOR VARIOUS ZINC BLENDE SEMICONDUCTORS.
EXPERIMENTAL HARDNESS VALUES SHOWN FOR COMPARISON.

	U_b (ev)	τ_p (kg/mm^2)	H_p (kg/mm^2)	H_{int} (kg/mm^2)	$H_p + H_{int}$ (kg/mm^2)	H_{exp} (kg/mm^2)
C	11.35	23,300	1940	9244	11,184	1
Si	5.95	3430	286	1098	1384	1370
Ge	6.67	3440	286	893	1179	1000
Sn	5.66	1930	161	---	---	----
AlP	6.04	3410	284	---	---	---
GaP	6.15	3500	292	903	1195	940
InP	5.78	2640	220	548	768	520
AlAs	5.90	3000	250	---	---	505
GaAs	6.03	3000	256	750	1006	580
InAs	5.64	2340	195	469	664	430
AlSb	5.08	2840	237	524	761	400
GaSb	5.36	2180	182	553	735	450
InSb	4.92	1670	139	365	504	230
ZnS	5.14	3000	250	515	765	----
CdS	4.77	2750	229	288	517	----
HgS	5.68	2590	216	---	---	----
ZnSe	4.92	2500	209	462	671	137
CdSe	4.59	1890	157	254	411	----
HgSe	4.53	1840	154	232	386	----
ZnTe	4.42	1720	143	374	517	82
CdTe	4.01	1350	113	222	335	60
HgTe	3.99	1360	113	230	343	25

Now we incorporate the Peierls energy into the hardness model for low temperature where the full barrier must be surmounted. The Sher model is based on energy considerations. The Vickers' hardness number is given by the applied force divided by the area of indentation. Multiplying the numerator and denominator by h, the depth of indentation we have $H = E/(W^2h)$, where $E = F \cdot h$ is the energy of indentation, and h is the depth of the indentation. Including the interaction energy only we have:

$$H = H_{int} = \frac{G \cot\theta}{6\pi(1-\nu)} \left[-\ln(\frac{\cot\theta}{2}) + \frac{4}{3} + \sin^2\frac{\theta}{2} \right]$$

where θ is one half the indenter angle. To include the Peierls energy, we consider the total energy necessary to move the dislocations from their initial to final positions in the idealized model. The hardness is then given by:

$$H = H_{int} + H_P$$

where

$$H_P = \frac{E_P}{W^2h}$$

is the Peierls contribution to the hardness, and E_P is the total Peierls energy expended. The total length of dislocation to be moved is calculated to be:

$$L_T = \frac{1}{6} \frac{W^3}{b^2} \cos^2\theta \quad .$$

The total Peierls energy is given by:

$$E_P = \frac{U_b}{b} L_T = \frac{1}{6} \frac{U_b W^3}{b^3} \cos^2\theta \quad .$$

15

Thus, we have:

$$H_P = \frac{1}{3} \frac{U_b}{b^3} \cos\theta \sin\theta \quad .$$

For $\theta = 45°$:

$$H_P = \frac{1}{6} \frac{U_b}{b^3} \quad .$$

Values of H_P are summarized in Table 3. Several features of H_P should be noted. First, we have used a zero temperature value of the Peierls energy. Because hardness measurements are typically done at room temperature, one should take the thermal energy into account, which will reduce the values of H_P from those listed in Table 3. Also shown in Table 3 are H_{int}, $H_{int}+H_p$, (the best theoretical estimate for H), and H_{exp}. Note that, like H_{int}, H_p is independent of the applied load, in agreement with experiment. Also note that H_p improves the agreement between theory and experiment for the hard, nonpolar materials. For the softer, more ionic materials, H is overestimated by the theory. We have begun to study the charge and polarity dependence of the dislocation motion, and expect that the over estimation of H is because of neglect of dislocation velocity effects and their temperature dependence, as discussed below.

3. Temperature Dependence

We have begun to develop a theory of the explicit temperature dependence of hardness. Here we summarize the experimental results and discuss a tentative theory of the temperature dependence.

Several recent studies on the temperature dependence of hardness serve to illustrate the behavior. Results for GaAs and Ge are shown in Figure 4. The (111) and (100) faces of GaAs have been examined by Hirsch et al.,[23] and Guruswamy et al.,[24] respectively. Results for the Knoop hardness on the (100) face of n-type Ge are also shown.[25] The (100) face of

16

1000

100

H — kg/mm²

10

O Roberts et al. (1986); Ge [100] , n-type

● Guruswamy et al. (1986); GaAs [100]

□ Hirsh et al. (1985); GaAs [111] A face

■ Hirsh et al. (1985); GaAs [111] B face

0   0.001   0.002   0.003

$\frac{1}{T} - \cdot K^{-1}$
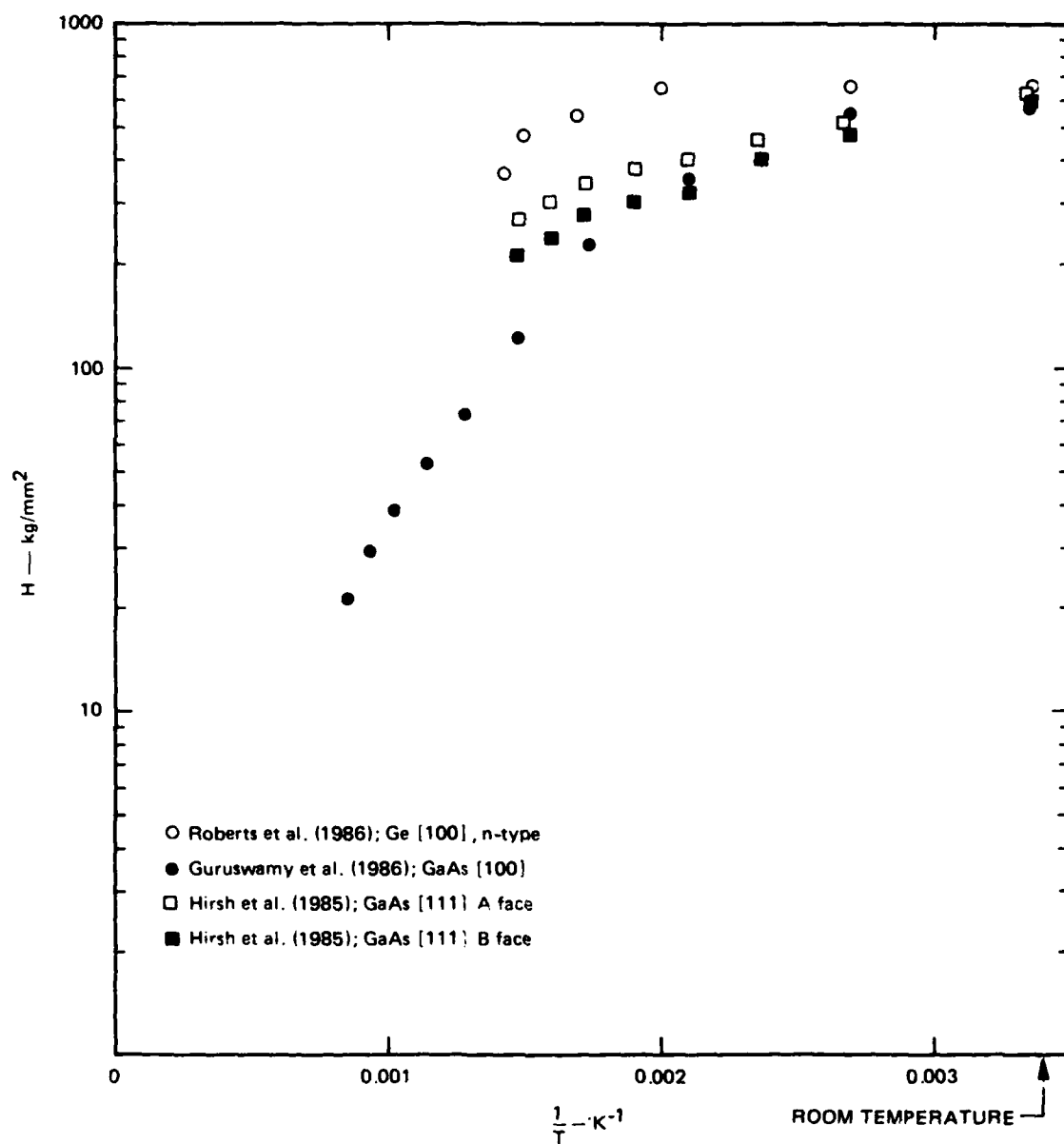
ROOM TEMPERATURE

FIGURE 4   TEMPERATURE DEPENDENCE OF HARDNESS FOR GaAs AND Ge

GaAs and the Ge show a definite temperature dependence with a relatively temperature independent region for T < 450K and an exponential temperature dependence for T > 550 K:

$$H = H_0 \, e^{\frac{U}{kT}}$$

with

$$U \cong 0.24 \text{ eV}$$

for (100) GaAs. The results for GaAs (111) appear to follow similar behavior.

The temperature dependence of hardness suggests that two different mechanisms may determine hardness in the two temperature regimes. At low temperature, the hardness is nearly independent of temperature and may be limited primarily by dislocation interactions. Dislocation mobility is low at low temperatures, and the tendency for dislocation pile-up is high. At elevated temperature, the dislocation mobility is increased, so that dislocations move more readily under an applied stress. Therefore, at higher temperatures, dislocation pile-up is reduced and the hardness is limited by lattice friction, which shows a strong temperature dependence. We are currently investigating a quantitative theory of the temperature dependence of hardness, which also includes the dissimilar velocities of the α and β dislocations.

C. Cleavage and Fracture

One of the basic ingredients to the calculation of the fracture properties in real materials is the cleavage energy. For ideal brittle fracture, i.e., fracture unaccompanied by crack tip blunting, dislocation generation, and phonon generation, the cleavage energy provides a good estimate of the fracture energy.

A simple model is usually used to calculate the cleavage energy, ε, based on the energy to separate two halves of a semiconductor crystal. That is:

$$\varepsilon = \int_0^{\delta_m} \sigma(x) dx$$

where $\sigma(x)$ is the restoring force per unit area for the crystal halves separated by a distance x, where x = 0 is the equilibrium position. We have begun to develop a method to calculate $\sigma(x)$, based on the cleavage of a crystal of infinite extent. This involved the calculation of the total energy of two semi-infinite crystals as a function of their separation. Based on a tight-binding theory, the cleavage energy, $\lim_{x \to \infty} \varepsilon(x)$, can be written as:

$$\varepsilon(x) = \varepsilon_{el} + V_0 + \varepsilon_{coul}$$

where ε_{el} is the change in the electron energies, V_o is the sum of the repulsive pair energies between the atom pairs across the interface, and ε_{coul} is the Coulomb energy, important for cleavage on polar surfaces. It is ε_{coul} that is difficult to calculate accurately; ε_{el} can be calculated systematically using the theory of the interface Green's function we have developed. A summary of this method follows.

The theory of surface Green's function has been developed for general layered structures, where, for the present case of cleavage, the layers are considered parallel to the cleavage surface. For a given crystal surface direction, here assumed to be the {110} cleavage plane, all the Green's functions are $\vec{k}_{//}$-dependent. That is:

$$\varepsilon_{el} = \sum_{\vec{k}_{//}} \varepsilon_{el}(\vec{k}_{//})$$

where

$$\varepsilon_{el}(\vec{k}_{//}) = \int_{-\infty}^{\varepsilon_f} \Delta\rho(\vec{k}_{//},E)EdE + \sum_i \Delta N_i \varepsilon_i$$

where E is the energy and ε_f is the Fermi energy, and where

$$\Delta\rho(\vec{k}_{//},E) = \sum_n \Delta\rho_n(\vec{k}_{//},E)$$

19

where n is the layer index and varies from $-\infty$ to $+\infty$, and the ε_i are possible localized states at the surface. The cleavage is assumed to occur between the layers $n = 0$ and $n = 1$. $\Delta\rho_n (\vec{k}_{//},E)$ is given by:

$$\Delta\rho_n(\vec{k}_{//},E) = -\frac{1}{\pi} \left[\text{Im}G_{nn} - \text{Im}g_{nn} \right] \quad .$$

G_{nn} and g_{nn} are the interface and surface Green's functions, respectively. These Green's functions are both $\vec{k}_{//}$ and energy dependent. The calculation of these Green's functions are straight forward and work has begun on setting up the problem for the {110} surfaces in zinc-blende semiconductor compounds. The calculation of this cleavage energy is simplified by the fact that the {110} surfaces are nonpolar.

V CONCLUSIONS

The major conclusions of our work are summarized below:

- Semiconductor alloys are never truly random, and deviations from randomness have been calculated for many III-V and II-V compounds.

- Deviations from random alloys are driven by excess energies due to bond-length differences, chemical differences, and polarity-induced Coulomb-energy differences between the constituents, and by externally applied coherent strain fields and temperature gradients. The correlation status might be growth-method dependent.

- Coulomb energies for ordered structures are smaller than for random alloys because of a Madelung enhancement in the ordered structures.

- Bond polarities have been calculated in excellent agreement with experiment.

- Vacancy formation energies in the semiconductor compounds are found to be surface-orientation dependent.

- Vacancy formation energies in the semiconductor alloys are found to vary nonlinearly with the near-neighbor alloy composition. Several possible consequences of this are:

  - Composition- and correlation-state dependent vacancy chemical potentials: multiple-vacancy-activation energies and entropies, and anomalous concentrations.

  - Anomalous diffusion: multiple-diffusion-activation energies, and entropies; parallel-path diffusion through percolating channels.

- A new effective medium theory predicts an approximately linear variation of the bulk modules with alloy composition.

- A foundation for the reduction from three to two-parameter force-constant models intetrahedrally coordinated has been established via an *ab initio* theory.

- The model of hardness has been improved by including the Peierls energies into the model.

- A theory of surface segregation has been initiated that shows surfaces:

  - Above T_c (the critical spinodal temperature) that are rich in one component and where the concentration returns to the bulk concentration in a few atomic layers.

  - Below T_c in which preliminary results show that the concentration oscillates back to the bulk value over many lattice spacings. This is a superlattice.

21

REFERENCES

1. A. Sher, M. van Schilfgaarde, A.-B. Chen, and W. Chen, "Quasichemical approximation in binary alloys," *Phys. Rev. B,* Vol. 36, p. 4279, 1987.

2. A. Sher, A.-B. Chen, M. van Schilfgaarde, and M.A. Berding, "Semiconductor alloys: structural property engineering," *Proc. 1st International SAMPE Electronics Conference (23-25 June 1987, Sunnyvale, California),* p. 323, 1987.

3. A. Sher, M.A. Berding, S. Krishnamurthy, M. van Schilfgaarde, A.-B. Chen, and W. Chen, "Structure-property relationships in semiconductor alloys," *Mat. Res. Soc. Symp. Proc.* Vol. 90, 91 (1987c)

4. A. Sher, M.A. Berding, M. van Schilfgaarde, A.-B. Chen, and R.S. Patrick, "Modeling of mechanical properties of II-VI materials," *J. Cryst. Growth,* Vol. 86, p. 15, 1988.

5. R.S. Patrick, A.-B. Chen, A. Sher, and M.A. Berding, "Phase diagrams and microscopic structures of (Hg,Cd)Te, (Hg,Zn)Te, and (Cd,Zn)Te alloys," *J. Vac. Sci. Tech. A,* Vol. 6, p. 2643, 1988.

6. M.A. Berding, A. Sher, A.-B. Chen, and W.E. Miller, "Structural properties of bismuth-bearing semiconductor alloys," *J. Appl. Phys.,* Vol. 63, p. 107, 1988.

7. R.S. Patrick, A.-B. Chen, and A. Sher, "Phase diagrams and local correlations in pseudo-binary alloys," *Phys. Rev. B,* Vol. 36, p. 6585, 1987.

8. G.B. Stringfellow, and P.E. Greene, *J. Phys. Chem. Solids,* Vol. 30, p. 1779, 1969.

9. M. vanSchilfgaarde, A.-Ban Chen, and A. Sher, "Coulomb energy in pseudobinary alloys," *Phys. Rev. Lett.,* Vol. 57, p. 1149, 1986.

10. M. van Schilfgaarde, A.-Ban Chen, and A. Sher, "Configuration dependence of coulomb interactions in pseudobinary alloys," *Proceedings of the 1986 7th International Conference on Ternary and Multinary Compounds, 10-12 September Snowmass, Colorado,* p. 411, 1987.

11. T.S. Kuan, T.F. Kuech, W.I. Wang, and E.L. Wilkie, *Phys. Rev. Lett.*, Vol. 54, p. 201, 1985.

12. M.A. Berding, A. Sher, A.-B. Chen, "Vacancy formation energies in II-VI semiconductors," *J. Vac. Sci. Technol. A*, Vol. 5, p. 3009, 1987.

13. M.A. Berding, A.-B. Chen, and A. Sher, "HgCdTe versus HgZnTe: Electronic properties and vacancy formation energies," *Mat. Res. Soc. Symp. Proc.*, Vol. 90, p. 127, 1987.

14. M.A. Berding, A. Sher, A.-B. Chen, "Vacancy formation energy in semiconductor compounds," submitted to Physical Review B.

15. M.A. Berding, A. Sher, A.-B. Chen, "Vacancy formation energy in semiconductor alloys," in preparation.

16. R.S. Patrick, A.-B. Chen, A. Sher, and M.A. Berding, "Surface Segregation in Pseudobinary Alloys," in preparation.

17. P.N. Keating, "Effect of invariance requirements on the elastic strain energy of crystals with application to the diamond structure," *Phys. Rev.*, Vol. 145, p. 637, 1966.

18. M. van Schilfgaarde, and A. Sher, "Tight-binding theory and elastic constants," *Phys. Rev. B*, Vol. 36, p. 4375, 1987.

19. M. van Schilfgaarde, and A. Sher, "Tight-binding theory of force constant models," *Appl. Phys. Lett.*, Vol. 51, p. 175, 1987.

20. A.-B. Chen, A. Sher, and M.A. Berding, "Semiconductor alloy theory: Internal strain energy and bulk modulus," *Phys. Rev. B*, Vol. 37, p. 6285, 1988.

21. F.A. McClintock, and A.S. Argon, *Mechanical Behavior of Materials*, Addison-Wesley, 1966.

22. A. Sher, A.-B. Chen, and W.E. Spicer, "Dislocation energies and hardness of semiconductors," *Appl. Phys. Lett.*, Vol. 46, p. 54, 1985.

23. P.B. Hirsch, P. Pirouz, S.G. Roberts, and P.D. Warren, "Indentation Plasticity and Polarity of Hardness on (111) Faces of GaAs," *Philos. Mag. B*, Vol. 52, p. 759, 1985.

24. S. Guruswamy, J.P. Hirth, K.T. Faber, "High Temperature Hardness of $Ga_{1-x}In_xAs$," *J. Appl. Phys.*, Vol. 60, p. 4136, 1986.

25. S.G. Roberts, P.D. Warren, and P.B. Hirsch, "Knoop Hardness Anisotropy on (001) Faces of Germanium and GaAs," *J. Mater. Res.*, Vol. 1, p. 162, 1986.

BIBLIOGRAPHY

M. vanSchilfgaarde, A.-Ban Chen, and A. Sher, "Coulomb energy in pseudobinary alloys," *Phys. Rev. Lett.*, Vol. 57, p. 1149, 1986.

M.A. Berding, A. Sher, A.-B. Chen, "Vacancy formation energies in II-VI semiconductors," *J. Vac. Sci. Technol. A*, Vol. 5, p. 3009, 1987.

M.A. Berding, A. Sher, and A.-B. Chen, "Polarity in Semiconductor Compounds," *Phys. Rev. B*, Vol. 36, p. 7433, 1987.

M.A. Berding, A.-B. Chen, and A. Sher, "HgCdTe versus HgZnTe: Electronic properties and vacancy formation energies," *Mat. Res. Soc. Symp. Proc.*, Vol. 90, p. 127, 1987.

A.-B. Chen, M. van Schilfgaarde, S. Krishnamurthy, M.A. Berding, A. Sher, "Alloy electronic structure and statistics," *Proceedings of the 1986 7th International Conference on Ternary and Multinary Compounds, 10-12 September Snowmass, Colorado*, p. 377, 1987.

R.S. Patrick, A.-B. Chen, and A. Sher, "Phase diagrams and local correlations in pseudobinary alloys," *Phys. Rev. B*, Vol. 36, p. 6585, 1987.

A. Sher, M.A. Berding, S. Krishnamurthy, M. van Schilfgaarde, A.-B. Chen, and W. Chen, "Structure-property relationships in semiconductor alloys," *Mat. Res. Soc. Symp. Proc.*, Vol. 90, p. 91, 1987.

A. Sher, A.-B. Chen, M. van Schilfgaarde, and M.A. Berding, "Semiconductor alloys: structural property engineering," *Proc. 1st International SAMPLE Electronics Conference, Sunnyvale, California*, p. 323, 1987.

A. Sher, M. van Schilfgaarde, A.-B. Chen, and W. Chen, "Quasichemical approximation in binary alloys," *Phys. Rev. B*, Vol. 36, p. 4279, 1987.

M. van Schilfgaarde, A.-Ban Chen, and A. Sher, "Configuration dependence of coulomb interactions in pseudobinary alloys" *Proceedings of the 1986 7th International Conference on Ternary and Multinary Compounds, 10-12 September Snowmass, Colorado*, p. 411, 1987.

M. van Schilfgaarde and A. Sher, "Tight-binding theory and elastic constants," *Phys. Rev. B*, Vol. 36, p. 4375, 1987.

M. van Schilfgaarde and A. Sher, "Tight-binding theory of force constant models," *Appl. Phys. Lett.*, Vol. 51, p. 175, 1987.

M.A. Berding, A. Sher, A.-B. Chen, and W.E. Miller, "Structural properties of bismuth-bearing semiconductor alloys,q *J. Appl. Phys.*, Vol. 63, p. 107, 1988.

A.-B. Chen, A. Sher, and M.A. Berding, "Semiconductor alloy theory: Internal strain energy and bulk modulus," *Phys. Rev. B*, Vol. 37, p. 6285, 1988.

R.S. Patrick, A.-B. Chen, A. Sher, and M.A. Berding, "Phase diagrams and microscopic structures of (Hg,Cd)Te, (Hg,Zn)Te, and (Cd,Zn)Te alloys," *J. Vac. Sci. Tech. A*, Vol. 6, p. 2643, 1988.

A. Sher, M.A. Berding, A.-B. Chen, and R. Patrick, "Stability of Alloy Semiconductors: Common Tellurium Anion II-IV Semiconductor," presented at "The Future of Small Gap II-VI Semiconductors," Univ. de Liege, Belgium, September, 1988.

A. Sher, M.A. Berding, M. van Schilfgaarde, A.-B. Chen, and R.S. Patrick, "Modeling of mechanical properties of II-VI materials," *J. Cryst. Growth*, Vol. 86, p. 15, 1988.

M.A. Berding, A. Sher, A.-B. Chen, "Vacancy formation energy in semiconductor compounds," submitted to Physical Review B.

A.-B. Chen, Y.-M. Lai-Hsu, and W. Chen, "Difference-equation approach to the electronic structures of surfaces, interfaces and superlattices," submitted to Physical Review B.

M.A. Berding, A. Sher, A.-B. Chen, "Vacancy formation energy in semiconductor alloys," in preparation.

R.S. Patrick, A.-B. Chen, A. Sher, and M.A. Berding, "Surface Segregation in pseudobinary alloys," in preparation.